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M. Zawadzki and A. Ragauskas

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Quantitative Determination of Quinone Chromophores in Isolated Lignins.

*Michael Zawadzki and Arthur Ragauskas,
Institute of Paper Science and Technology,
500 10th St. NW, Atlanta, Georgia 30318.*

Abstract

Quinone substructures in lignin are important chromophores which are thought to negatively impact brightness development during industrial pulp bleaching. In this paper, a trimethylphosphite derivatization procedure is presented for the quantitative determination of lignin-quinone contents. Lignins investigated were isolated from chlorine dioxide, oxygen, alkaline extraction, and peracetic acid bleached pulps. Chlorine dioxide dramatically increased lignin-quinone content whereas subsequent alkaline extraction reduced the content. Oxygen delignification also resulted in quinone introduction, but to a lesser extent than with chlorine dioxide. Peracetic acid displayed a beneficial effect by eliminating quinone structures. Trimethylphosphite derivatization chemistry was investigated with small molecule benzoquinones and oxidized poly(4-vinylphenol). Generally small molecule benzoquinones were derivatized in good yield, except, 3-methoxy-1,2-benzoquinone gave less than complete derivatization due to competing self-dimerization. Conditions necessary for optimum derivatization yield of isolated lignins, removal of trimethylphosphite degradation products, and quantitative NMR analysis are also discussed.

Introduction

The goals of kraft pulp bleaching are twofold: delignification, or removal of bulk residual lignin, and brightening. Generally, the lignin component may cause as much as 90% of

the visible region light absorption coefficient of unbleached kraft pulps [1]. The production of high value paper products relies upon bleaching pulps to high brightness. Therefore, knowledge of the fundamental chemistry of both brightening and delignification stages are crucial. Pulp delignification chemistry has been extensively studied [2-5]. Unfortunately, fundamental knowledge of lignin and chromophore transformations during brightness development are much less developed.

Surprisingly, the structures responsible for color in mechanical and chemical pulps are only qualitatively known. Various studies have suggested that colored substructures present in the lignin macromolecule may include: quinone-methides [6], stable radicals [7], stilbenes [7, 8], conjugated carbonyls, and/or benzoquinones [6, 9-11].

Benzoquinones occur as either *ortho* (1,2-) or *para* (1,4-) forms, and are highly colored, λ_{\max} 420–580 nm [12]. It has often been suggested that quinones are involved in the yellowing of mechanical pulp [7, 13, 14]. Also, the color of kraft [9] and soda lignin [15, 16] has been attributed to the presence of benzoquinone structures. Lignin-quinones may arise during the alkaline pulp cooking process from methyl-aryl ether cleavage after subsequent air oxidation of phenolic units [5, 15, 16].

Benzoquinone structures play an important role in both chlorine dioxide and hydrogen peroxide bleaching processes. Chlorine dioxide has been demonstrated to react with phenolic lignin model compounds to give *ortho*- and *para*-benzoquinone products [17-19]. Hydrogen peroxide, conversely, acts as a powerful brightening agent by eliminating conjugated carbonyl structures, including quinones [3, 20]. Recently, Zawadzki *et al.* quantified the quinone contents of residual lignins isolated from chlorine dioxide bleached pulps (DE*DED) [21, 22]. Lignin-quinone levels were found to correlate with pulp brightness and brightness ceiling values, suggesting that quinones negatively impact brightness development [21].

Although lignin-quinones are widely acknowledged to be important chromophores, until recently few reliable methodologies were available for the quantitative analysis of these structures in lignocellulosic materials [23]. Visible absorption spectroscopy is not directly effective for lignin-quinone quantification because of the broad featureless nature of lignin absorption spectra [24]. Classical colorimetry-based [23] and hydrazine oxidation [23] methods of quinone measurement are difficult to apply. *Ortho*-

phenylenediamine derivatization and fluorescence spectroscopy has been used for the determination of *ortho*-benzoquinone structures in mechanical pulps [25, 26]. Unfortunately, the technique is not applicable for the analysis of important *para*-benzoquinone structures.

Recently, ^{19}F -NMR-based spectroscopic techniques have been developed for the analysis of quinone structures in isolated lignins. 4-trifluoromethylphenylhydrazine derivatization/ ^{19}F -NMR was applied for quinone analysis on a range of isolated lignins [27, 28]. Alternatively, derivatization by Ruppert's reagent has been suggested for lignin-carbonyl analysis [29], but model compound studies have revealed overlap between *para*-quinone and aldehyde derivatives [30].

A number of reports have described trimethylphosphite (TMP) derivatization of mechanical pulps. TMP has been reported to specifically form adducts with *ortho*-quinone structures [31-35]. Lebo *et al.* were first in applying TMP derivatization and phosphorus microanalysis for *ortho*-quinone quantification during mechanical pulp photoyellowing [31, 32]. Similarly, Konya and Scaiano employed a trialkylphosphite-based derivatization procedure to detect *ortho*-quinones by fluorescence spectroscopy [33]. Argyropoulos *et al.* used solid-state ^{31}P -NMR and TMP derivatization to qualitatively monitor *ortho*-quinone levels in a range of mechanical pulps [34]. Argyropoulos *et al.* also reported that carboxylic acid groups, but not carboxylic acid salts, interfere with solid-state ^{31}P -NMR analysis of quinones [35].

Recent investigations of TMP derivatization has revealed that both *ortho*- and *para*-benzoquinone structures in lignins can be quantified simultaneously. The fundamental chemistry of the method has been verified by model compound studies [22, 36-38]. The combined *ortho*- and *para*-quinone contents of isolated lignins can readily be detected by TMP derivatization and ^{31}P -NMR spectroscopy [21, 22, 28, 37]. Similarly, Argyropoulos and Zhang have shown the application of TMP derivatization on a variety of isolated lignin samples [36]. Recently, Zhang and Gellerstedt applied the methodology towards the analysis of milled-wood lignin samples [39].

This paper describes our ongoing research utilizing TMP derivatization and ^{31}P -NMR spectroscopy as a tool for quantitative analysis of quinone structures in isolated lignins. The purpose of this study was to optimize quinone derivatization conditions and

understand the TMP derivatization and degradation chemistries. Then, the developed procedure was applied for the analysis of residual lignins isolated from chlorine dioxide, oxygen, alkaline extraction and peracetic acid bleached pulps.

Experimental Section

All chemicals were purchased commercially and used without further purification, unless otherwise noted. 4-methyl-1,2-benzoquinone, 4-*tert*-butyl-1,2-benzoquinone, 3-methoxy-1,2-benzoquinone, and 2-*tert*-butyl-1,4-benzo-quinone were prepared by silver oxide oxidation of the analogous catechols and hydroquinone using the method of Cason [40]. Poly(4-vinylphenol) (PVP, MW ~ 22,000), enriched in quinone content, was prepared by Fremy's reagent oxidation according to a procedure modified from the literature [41]. Structures of quinone model compounds are illustrated in Figure 1.

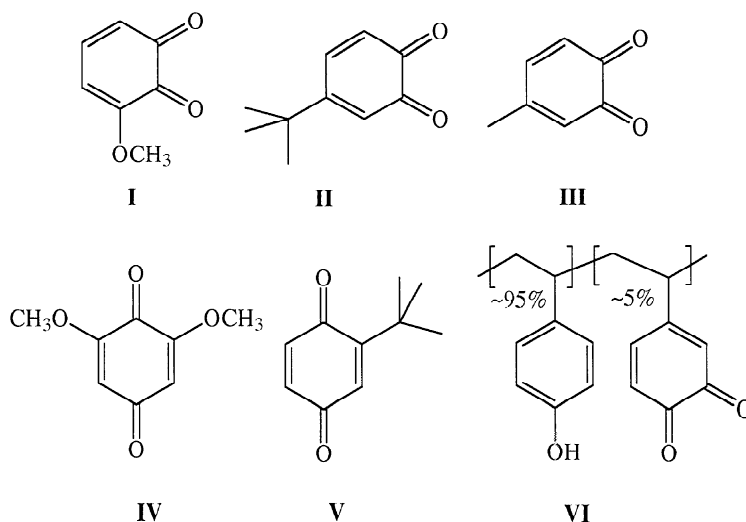


Figure 1. Structures of model compounds studied.

Chlorine dioxide (D) and alkaline extracted (E) pulps were bleached as previously described [42]. Both conventional ($\kappa = 28$) and EMCCTM ($\kappa = 29$) laboratory softwood kraft pulps were used. Chlorine dioxide bleaching was performed in a Quantum Technologies mixer at 45°C, 10% consistency, using a kappa factor of 0.2 and a 30–

minute reaction [42]. The alkaline extraction stage was performed in a peg mixer at 70°C, 10% consistency, using ~1.2% NaOH charge and a 60-minute reaction.

Oxygen delignified and peracetic acid treated pulps were prepared as previously described [43]. A laboratory softwood polysulfide/anthraquinone (PS/AQ) kraft pulp ($\kappa = 45.4$) was used [43]. Oxygen delignification was accomplished in a peg mixer at 110°C, with ~1.1% NaOH charge, using 70 psig oxygen pressure and a 60-minute reaction [43]. Equilibrium peracetic acid treatment was performed at 80°C using a 6% charge and 60-minute reaction.

Lignins were isolated from bleached pulps by an acidic 1,4-dioxane isolation procedure previously reported [42, 44]. Lignin was extracted from the pulp with 90% 1,4-dioxane/0.1 N HCl (v/v) solution (10% consistency) by refluxing for 2 hours under an argon atmosphere. The mixture was then filtered, concentrated, and purified by precipitation. Isolated lignin yield was approximately 30–46% relative to pulp κ number [42, 43]. Purified lignin was freeze-dried and used for further analysis.

Dry model compounds (0.2 mmol) and lignin (30 mg) were derivatized with 250 μ L TMP and 250 μ L anhydrous solvent under an argon atmosphere at room temperature for two days. TMP was previously purified by distillation from sodium metal. The following derivatization solvents were studied: dimethylformamide (DMF), DMF containing 2% water, and dimethylsulfoxide (DMSO). Derivatized samples were prepared for analysis by removing excess TMP under vacuum at 40°C. Then, 250 μ L DMSO was added and the sample was placed under vacuum at 50°C until nearly dry.

Derivatized model compounds were dissolved in 450 μ L of DMSO- d_6 containing 19.3 mg/mL tri-*meta*-tolylphosphate (TTP) and 6.0 mg/mL chromium-acetylacetonate ($\text{Cr}(\text{acac})_3$). Treated lignins were dissolved in 450 μ L of DMSO- d_6 containing TTP (0.84 mg/mL) and $\text{Cr}(\text{acac})_3$ (1.0 mg/mL). Derivatized samples were hydrolyzed by the addition of water (10 μ L for model compounds and 5 μ L for lignin).

Phosphorus-NMR spectra were acquired with a Bruker 400 MHz NMR spectrometer using the following quantitative conditions: 90° pulse, 5-second pulse delay, inverse-gated broadband proton decoupling, 64K time domain, and one degree of zero filling. For treated model compounds 100–400 scans/spectrum were collected. For treated lignin 2000 scans/spectrum were collected. The internal standard, TTP, gave a sharp

resonance at δ -16.3 ppm (vs. 85% H_3PO_4) and was used for quantitative analysis and as a shift reference. To ensure quantitative spectral acquisition, the pulse delay exceeded five times the longest measured spin-lattice relaxation time.

Results and Discussion

Derivatization Chemistry. Trivalent phosphorous compounds, particularly trialkylphosphites, are well known to react specifically with *ortho*- and *para*-quinones. The chemistry of TMP reactivity with quinone structures has been extensively studied by Ramirez and others [45-48].

In recent years, interest in detecting quinones in lignocellulosic materials has led to a reexamination of TMP/quinone derivatization chemistry. Shown in Figure 2 is the reaction of the *ortho*-quinone model compound 3-methoxy-1,2-benzoquinone (I) with TMP. The initial stages of TMP/quinone derivatization are obscure, but electron spin resonance spectroscopy has revealed that the reaction may proceed by a radical mechanism [49].

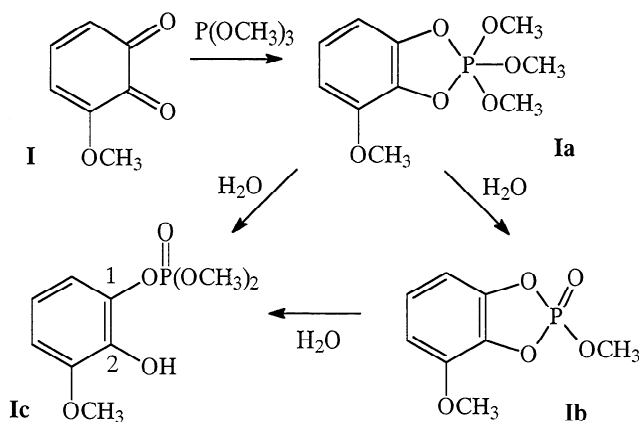


Figure 2. Reaction of TMP with 3-methoxy-1,2-benzoquinone.

Regardless of the initial mechanism of phosphorus attack, cyclization occurs and a benzodioxaphospholene structure (Ia, Figure 2) is formed [46]. The benzo-dioxaphospholene adduct can readily be detected by ^{31}P -NMR spectroscopy at approximately

δ -45 ppm. Many reports have extensively documented this facile reaction on a variety of *ortho*-quinone compounds [22, 36-38, 47, 48, 50].

Dioxaphospholene structures are known to be unstable towards both water and oxygen [47, 51]. We envisioned that practical TMP derivatization of lignin would likely involve unavoidable exposure to water. Therefore, understanding the hydrolysis chemistry of benzodioxaphospholenes is critical for the development of a robust quinone analysis method.

The literature contains a number of reports regarding the hydrolysis of dioxaphospholene structures with water. Early reports by Ramirez [46, 52, 53] indicated that the addition of water to aliphatic-diketone derived dioxaphospholenes resulted in nearly quantitative conversion to the cyclic phosphate ester (analogous to Ib, Figure 2, δ ~12 ppm, *cf.* [54]). Later, studies of the hydrolysis reaction on related substrates found complete hydrolysis to the open-chain phosphate ester form (analogous to Ic) [47, 55, 56].

Until recently, few hydrolysis studies on (*ortho*-quinone-derived) benzodioxaphospholene structures have been reported. Kirillova and Kukhtin found that the hydrolysis of dioxaphospholenes derived from TMP/1,2-naphthoquinones gave predominantly the dimethyl-phosphate ester with little cyclic phosphate adduct [57]. A number of workers, including this group [22, 37], have recently confirmed that TMP derivatization of *ortho*-quinones, followed by hydrolysis, yields stable dimethylphosphate ester products and negligible cyclic phosphate ester content [36, 38, 48, 50, 57].

For 3-methoxy-1,2-benzoquinone, the stable products of hydrolysis are two dimethylphosphate esters (Ic, Figure 2) with resonances at δ -2.0 and δ -2.7 ppm (Table 1). Note, ring opening of the benzodioxaphospholene structure leads to either C1 or C2 substituted isomers (Ic, Figure 2). The chemical shifts of adduct(s) Ic compare favorably with δ -2.33 ppm reported in related studies (CDCl_3 solvent) [36, 50]. 4-*tert*-Butyl- and 4-methyl-1,2-benzoquinone were derivatized by TMP and also displayed adducts in the δ -2.5 ppm region (Table 1).

We further explored characterization of adduct Ic (Figure 2) by ^{31}P - ^1H heterocorrelation spectroscopy using the COLOC pulse sequence [58]. Selecting a phosphorus-proton spin coupling constant of 11.0 Hz, indicative of a POCH_3 moiety, we found the

Table 1. Chemical shifts for TMP–quinone adducts.

Benzoquinone	$\delta^{31}\text{P}$ (ppm) ^a
3-methoxy-1,2-benzoquinone (I)	-2.0, -2.7
4- <i>tert</i> -butyl-1,2-benzoquinone (II)	-2.3, -2.6
4-methyl-1,2-benzoquinone (III)	-2.4, -2.6
2,6-dimethoxy-1,4-benzoquinone (IV)	-1.6, -1.7
2- <i>tert</i> -butyl-1,4-benzoquinone (V)	-2.6, -2.7

^a chemical shift of dimethylphosphate ester products.

expected correlation between the phosphorus signal at δ -2.0 and -2.7 ppm with methoxyl proton, δ 3.8 ppm, thereby further supporting assignment of the adducts as dimethylphosphate esters (Figure 3).

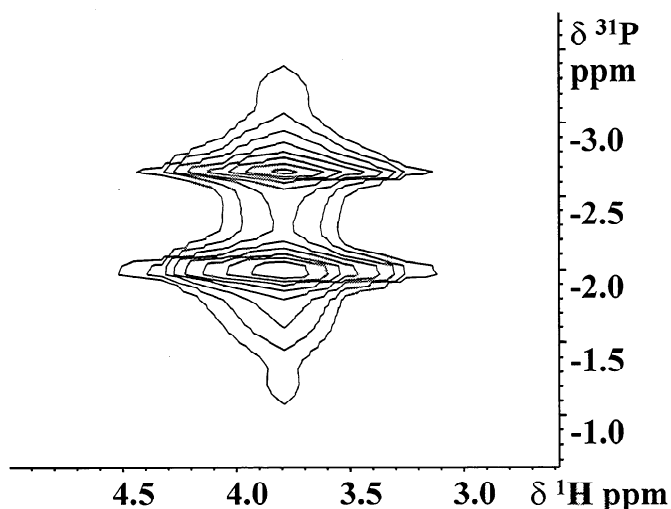


Figure 3. ^{31}P – ^1H heterocorrelation spectrum (COLOC) of TMP treated 3-methoxy-1,2-benzoquinone.

The reaction of TMP with *para*-benzoquinone structures has been well documented [22, 36, 37, 45-47, 50, 59-61]. In Figure 4 the reaction of TMP with 2-*tert*-butyl-1,4-benzoquinone (V) is shown. Initial attack of the phosphorus is reported to give a tetraalkoxyphosphonium intermediate. The intermediate (Va, Figure 4) is a very reactive alkylating agent (*cf.* [62]) and is readily degraded by water to the analogous hydroquinone (Vb, Figure 4) [60, 63, 64].

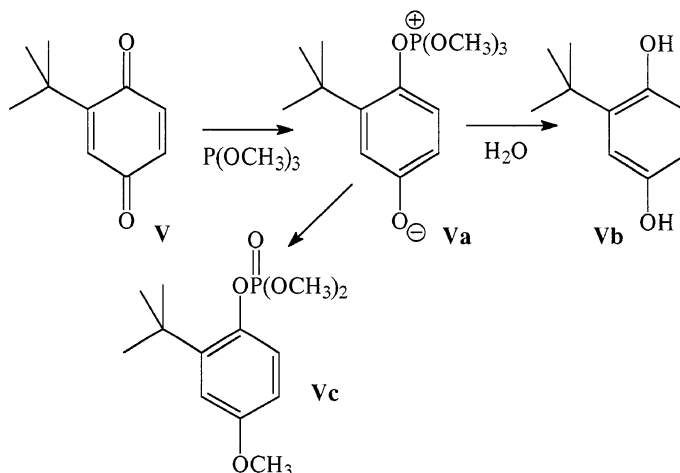


Figure 4. Reaction of TMP with 4-*tert*-butyl-1,4-benzoquinone.

If water is excluded from the reaction mixture, methyl group translocation to another molecule Va (Figure 4) gives the dimethylphosphate ester (Vc) in high yield [22, 36, 37, 59]. Note, although the reaction intermediate (Va, Figure 4) is hydrolytically unstable, the dimethylphosphate ester product(s) are stable to the presence of water [64]. As with the *ortho*-benzoquinone substrates, TMP derivatized *para*-benzoquinones may give two isomeric dimethylphosphate ester products. From Table 1, chemical shift data for the 2-*tert*-butyl- and 2,6-dimethoxy-1,4-benzoquinone derived phosphate esters were found at δ -1.6 to -2.7 ppm — in the same region as derivatized *ortho*-benzoquinones.

Yield Data. Table 2 lists dimethylphosphate ester yield data for TMP derivatized of *ortho*- and *para*-benzoquinone model compounds. The initial derivatization conditions involved 50% TMP/DMF treatment for two days. The most sterically hindered benzoquinones, II and IV (Table 2), were found to give high yield (>83.7%) of the desired dimethylphosphate adduct. Generally, the dimethylphosphate yield appeared to correlate with benzoquinone structure.

We suspected that lower derivatization yields observed for some benzoquinone compounds (Table 2) were related to instability of the model. Quinones are well known to be unstable to the presence of light [65] and can also undergo self dimerization *via* the Diels–Alder reaction ($4\pi + 2\pi$ cycloaddition) [66]. Note, when quinone I was merely

Table 2. Reaction yields of quinone compounds derivatized with TMP.

Benzoquinone	Yield ^a (%)
3-methoxy-1,2-benzoquinone (I)	53.5 (80.8 ^b , 22.2 ^c)
4- <i>tert</i> -butyl-1,2-benzoquinone (II)	83.7 (84.1 ^b)
4-methyl-1,2-benzoquinone (III)	69.9 (71.7 ^b)
2,6-dimethoxy-1,4-benzoquinone (IV)	95.7
2- <i>tert</i> -butyl-1,4-benzoquinone (V)	70.1
oxidized PVP (VI)	0.116 mmol/g
PVP	0.006 mmol/g

^a yield determined by ³¹P-NMR spectroscopy.

^b cooled to -52°C then treated with 100% TMP for 16 hr.

^c dissolved in DMF then after 24 hr treated with TMP for 2 days.

dissolved in DMF solvent (light excluded) for 24 hours before TMP derivatization, the yield was drastically lowered (22.2%, Table 2).

A series of *ortho*-benzoquinone compounds were studied using 100% TMP derivatization and, in all cases, the yield increased, especially so for 3-methoxy-1,2-benzoquinone (I, Table 2). For small *ortho*-benzoquinone compounds, derivatization yield may be dependent on the relative rates of self-dimerization and TMP derivatization. Although, small molecule quinones have been used to represent lignin-quinone structures [36-38], in some cases their ephemeral stability in solution may preclude extrapolation of the yield results to lignin-quinones. Nevertheless, sterically hindered benzoquinones, as described in this report (Table 2) and others [36-38], have given very high dimethylphosphate yields.

During the course of this investigation, PVP enriched with *ortho*-benzoquinone structures (VI, Figure 1) was prepared and derivatized by TMP (Table 2). An increase in quinone content, relative to unoxidized PVP, was noted. The estimated *ortho*-benzoquinone enrichment was ~5% of the monomer units. Polymeric quinones such as oxidized PVP should serve as realistic models for lignin-quinones. Like lignin, quinone substructures in oxidized PVP are present at low level in a low mobility matrix. Dimerization reactions should be much less likely to occur than with small molecule

quinones. Further work is in progress to verify the quinone content data determined for the oxidized PVP by an alternative method.

TMP Degradation Products. Trialkyl- and triaryl-phosphites are well known to degrade to hydrogen-phosphite, $(\text{RO})_2\text{P}(=\text{O})\text{H}$, structures by the action of water or acids [67-69]. Potentially during TMP (VI, Figure 5) treatment of lignin, dimethylphosphite $(\text{CH}_3\text{O})_2\text{P}(=\text{O})\text{H}$ may form because of the presence of traces of water in the reaction mixture and/or lignin-acid or hydroxyl functional groups (VI→VII, Figure 5). Methyl-dimethylphosphonate (IX, Figure 5) is a degradation product that can arise by a facile Arbuzov rearrangement of TMP [70, 71]. TMP oxidation by air, particularly in the presence of quinones [72], can give trimethylphosphate (VIII, Figure 5) [22, 36-38]. Ideally, degradation products from TMP should either be noninterfering or removed prior to quinone analysis.

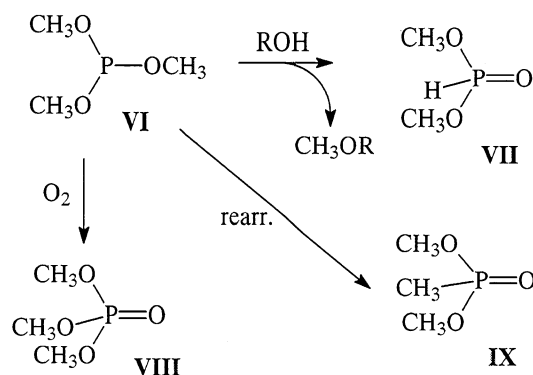


Figure 5. TMP degradation scheme.

Although the concentration of degradation products in the TMP reagent is low, their presence can make quinone analysis particularly challenging. An understanding of the potential interference of TMP degradation products is especially important in connection with lignin-quinone analysis in which the quinone content is very low.

Figure 6 illustrates a ^{31}P -NMR spectrum of TMP and its degradation products (DMSO- d_6 solvent). Chemical shifts and ^{31}P - ^1H coupling constants for TMP-derived structures are given in Table 3. Clearly, all degradation products, as illustrated in Figure 5, are observed in the spectrum (Figure 6). The component with a chemical shift at

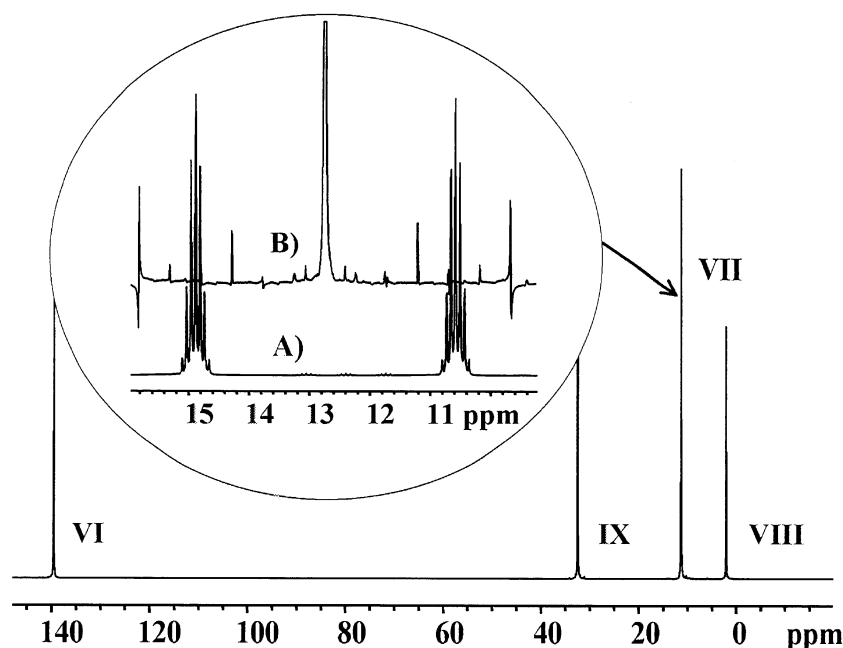


Figure 6. Proton decoupled ^{31}P -NMR spectrum of TMP and degradation products. Inset: A) Proton coupled, and B) Waltz-16 proton decoupled.

δ 12.6 ppm gives a doublet of two septets ($^3J_{\text{POCH}} = 12.1$ Hz) when observed with protons coupled (Figure 6A). The septet indicates the presence of two $-\text{OCH}_3$ groups directly bonded to phosphorus [73]. The large dispersion between the two septets is due to a 699.4 Hz coupling constant ($^1J_{\text{PH}}$), which is a unique signature for hydrogen-phosphites [74], arising from dimethylphosphite (Figure 6). The noted presence of dimethylphosphite is consistent with TMP hydrolysis.

Table 3. ^{31}P -NMR parameters for TMP related compounds.

δ ^{31}P (ppm) ^a	Lit. δ ^{31}P (ppm) ^e	Compound
140.9 (10.7 ^d)	140.9 (10.5–10.7 ^d)	trimethylphosphite (VI)
33.8 (17.5 ^c , 11.0 ^d)	29.1–32.3 (17.3 ^c , 10.9 ^d)	dimethylmethyl-phosphonate (IX)
12.6 (699.4 ^b , 12.1 ^d)	9.3–14.3 (710 ^b , 12 ^d)	dimethylphosphite (VII)
3.5 (11.1 ^d)	-2.4–2.4 (10.2–11.4 ^d)	trimethylphosphate (VIII)

^a DMSO- d_6 solvent, ~10% v/v, H_3PO_4 external standard
coupling constants: $^1J_{\text{PH}}$ (Hz) ^b, $^2J_{\text{PCH}}$ (Hz) ^c, $^3J_{\text{POCH}}$ (Hz) ^d

^e literature: [73-78]

Our experience has indicated that the presence of dimethylphosphite causes difficulty with trace quinone quantification. Proton decoupling is often used in ^{31}P -NMR spectroscopy because a increase in peak sharpness and sensitivity can be gained. Standard 1D ^{31}P (and ^{13}C) pulse sequences on modern NMR spectrometers typically use the Waltz-16 (^1H) decoupling scheme. Unfortunately, Waltz-16 ^1H decoupling of dimethylphosphite was found to introduce cycling sideband interference [79] into the spectrum (Figure 6 B). The decoupling artifacts can clearly be seen in Figure 6 B as spurious spikes symmetrical about the central resonance. The spurious resonances were observed to occur well within the δ -2 ppm region used to monitor benzoquinone derivatives.

Preliminary ^{31}P -NMR studies of TMP-derivatized lignin (containing dimethylphosphite) were found to suffer from severe cycling sideband interference when Waltz-16 ^1H decoupling was used. Two strategies were selected to give a robust method for trace quinone analysis. First, the negative influence of dimethyl-phosphite was substantially reduced by removing the volatile compound using vacuum and heat [21, 22, 37]. Second, residual dimethylphosphite was found to be effectively ^1H decoupled by using classical high-power broadband decoupling (Figure 6) instead of the Waltz-16 sequence. To further mitigate TMP degradation, quantitative derivatization was conducted under an argon atmosphere, in the dark, and using anhydrous solvents.

Quinone Contents of Isolated Lignins. We applied TMP derivatization/ ^{31}P -NMR analysis to a series of lignins isolated from bleached and unbleached kraft pulps. An important NMR parameter that must be evaluated prior to quantitative NMR acquisition is the spin-lattice (T_1) relaxation parameter. Typically five times the T_1 parameter is selected as the shortest pulse delay that may be used during quantitative NMR acquisition [80].

The applicable T_1 parameters were determined in this study on actual derivatized lignin samples and oxidized PVP (Table 4). Additionally, the T_1 parameter for the internal standard was determined at a concentration typical of routine analysis (Table 4). It should be noted that the T_1 parameter is a dynamic parameter that is influenced by a number of factors including: concentration of $\text{Cr}(\text{acac})_3$, sample concentration, solvent,

Table 4. Chemical shifts and spin–lattice relaxation times for TMP–quinone adducts.

Compound	$\delta^{31}\text{P}$ (ppm)	T_1 (sec) ^a
oxidized PVP	-2.7 ^b	0.70
TMP treated D ₀ (KF = 0.2, SW brownstock kappa = 29)	-2.5 ^b	0.70
TTP (0.84 mg/mL, 1.0 mg/mL Cr(acac) ₃)	-16.3	0.77 (0.75 ^c)

^a T_1 of dimethylphosphate adduct (~ -2 ppm) or TTP.

^b determined by lineshape analysis (NUTS, Acorn NMR).

^c in the presence of derivatized D₀ lignin (KF = 0.2, SW brownstock kappa = 29).

and others [80, 81]. Quantitative NMR acquisition can be assured for any of the samples listed in Table 4 when a 5-second (90°) pulse delay is used.

Table 5 gives quinone content data for a series of residual lignins isolated from bleached pulps. Referring to item X (Table 5), the lignin–quinone content was measured after 2 and 7 days of TMP treatment. The content measured after 2 days was 98% of the 7-day result, indicating that a 2-day reaction is sufficient for quantitative derivatization. Similarly, the quinone contents for various other isolated lignins also had second day values close to the 7 day result (>93%, XI, XIII, and XIV, Table 5). In a few cases, derivatization was studied using DMSO as a solvent instead of DMF (XII and XV–XVIII, Table 5) (*cf.* [21, 22, 28, 37]). The quinone content values were close in value when either solvent was used (XII, Table 5).

In a recent effort, Argyropoulos and Zhang found that the TMP derivatization yield of simple quinone compounds is ~70% when the reaction is performed in DMF containing both 0.5% water and lignin [36]. As a result of this experiment, they concluded that the measured quinone content of TMP derivatized lignin must be multiplied by 1.43 (i.e. 100/70) to give the actual content. From a review of the literature, the lower derivatization yield, observed by Argyropoulos and Zhang [36], is consistent with reports indicating that TMP, in the presence of water, acts as a quinone reducing agent [60, 63, 64].

To verify the hypothesis that water reduces derivatization yield, we derivatized a chlorine dioxide residual lignin using DMF solvent containing 2% water. The measured

Table 5. Quinone contents of TMP derivatized lignins.

	Residual Lignin	Quinone concentration (mmol/g lignin)	
		DMF (2-day) ^a	DMF (7-day) ^a
	<u>SW kraft pulps ^b:</u>		
X	D ₀ (KF = 0.2, EMCC TM BS kappa = 29)	0.241 (0.126 ^d)	0.245
XI	BS (kappa = 28)	0.067	0.072
XII	D ₀ (KF = 0.2, BS kappa = 28)	—	0.215 (0.220 ^c)
XIII	DE (KF = 0.05)	0.077	0.078
XIV	DE (KF = 0.2)	0.114 ± 0.004	0.123 ± 0.004
	<u>PS/AQ kraft pulps ^c:</u>		
XV	BS (kappa = 45)	—	0.028 ^c
XVI	O	—	0.074 ^c
XVII	OO	—	0.103 ^c
XVIII	OPa	0.056	0.058 ^c

— = not determined, ^a treatment time, ^b see Froass *et al.* [82], ^c 7 days 50% TMP/DMSO, ^d 2 days 50% TMP/DMF (2% water), ^e see Moe *et al.* [43].

quinone content was found to be 53% of the value when anhydrous DMF solvent was used (X, Table 5). Therefore, the use of both dry samples and reagents during TMP treatment are likely essential for quantitative derivatization.

Chlorine dioxide has been reported in several studies [17-19, 83-86] to oxidize phenolic lignin model compounds to *ortho*- and *para*-benzoquinone structures. Table 5 documents the dramatic introduction of colored lignin-quinone structures as a result of chlorine dioxide bleaching. Comparing residual lignins isolated from unbleached (XI, Table 5) and chlorine dioxide bleached (XII) pulps [82], a ~3-fold increase in the quinone is measured.

Increased lignin-quinone content after chlorine dioxide bleaching may be counterintuitive because it strongly suggests the bleaching stage darkens the lignin remaining in the pulp. In fact, by visible spectroscopy, we have demonstrated that chlorine dioxide

darkens lignin [22]. These results suggest that chlorine dioxide bleaching involves both productive lignin removal and counter-productive lignin darkening reactions.

Industrially, after chlorine dioxide bleaching, pulps are processed with an alkaline extraction stage. Residual lignins isolated from pulps at this stage showed a dramatically reduced quinone content (XIII and XIV, Table 5). The lower quinone content is consistent with reports indicating alkali degrades quinones to α -hydroxy-carboxylic acid structures *via* a benzylic acid-type rearrangement [3]. Alternatively, alkali can transform quinones into more highly colored hydroxy-quinone structures [3, 87] that may be resistant to subsequent bleaching operations.

Residual lignins, isolated from oxygen delignified and peracetic acid pulps [43], were also investigated. The quinone contents of residual lignin from the unbleached pulp (XV, Table 5) was found to be low. Oxygen (XVI) and double-stage oxygen (XVII) caused an increase in the measured quinone content, although not as dramatic as observed with chlorine dioxide. Peracetic acid was applied after oxygen delignification gave a beneficial reduction of the quinone content. This result is consistent with higher brightness, as previously reported [43] and its known chemistry [88].

Figure 7 illustrates ^{31}P -NMR spectra of TMP-derivatized chlorine dioxide residual lignin, oxidized PVP, and PVP. The broad Gaussian resonances (Figure 7), centered at $\delta \sim -2.5$ ppm (Table 4), are attributed to dimethylphosphate TMP/quinone adducts. Note, the resonances from derivatized quinone structures are well separated from down-field signals due to trimethylphosphate (VIII, Table 3) and other aliphatic phosphate esters. The reproducibility of quinone measurement was found to be $\pm 3.5\%$ using an alkaline extraction stage residual lignin (XIV, 2-day treatment, Table 5) derivatized in triplicate.

Quinone Content of Oxidized PVP. Factor and Donahue used TMP derivatization/ ^{31}P -NMR to qualitatively determine *ortho*-quinone structures in γ -irradiated bisphenol-A polycarbonate [89]. They monitored derivatized *ortho*-quinones as the unstable benzo-dioxaphospholene derivative (analogous to Ia, Figure 2). Their work confirmed the presence of quinones as potential colored bodies in these polymers. Similarly, this present study demonstrated the ability to quantify quinone structures in polymeric oxidized PVP

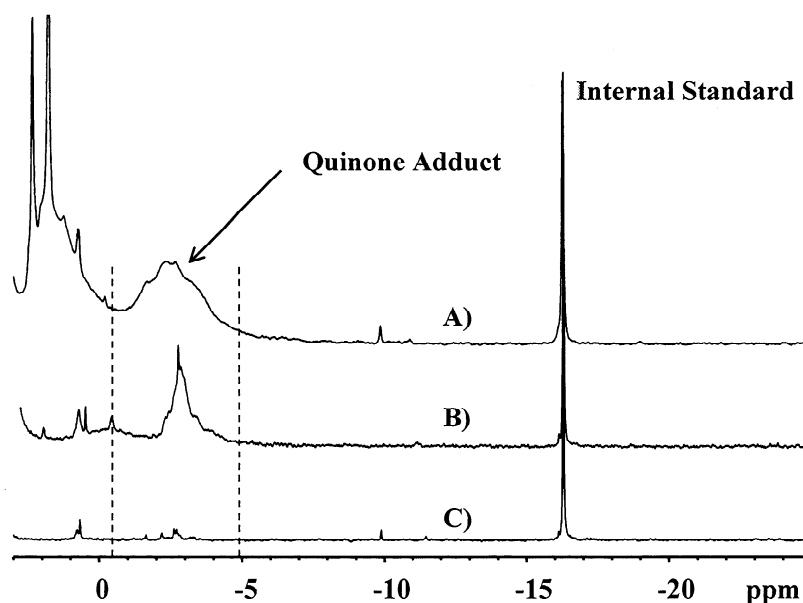


Figure 7. ^{31}P -NMR spectra of compounds treated with 50% TMP/DMF for 2 days: A) D_0 residual lignin, B) oxidized PVP, and C) PVP.

(Table 2 and Figure 7). Potentially, TMP derivatization may have broad applicability for the quantitative study of quinone contents in a variety of aromatic-based polymeric materials.

Secondary Lignin/TMP Reactions. Lignin is rich in a variety of hydroxyl functional groups, and our studies have indicated that a portion of these structures may form TMP-derived products. Identification of these "secondary" reaction products was critical because they may have been falsely attributed to quinone-TMP adducts.

Figure 8 reveals ^{31}P -NMR spectra of TMP-treated 3,4-dimethoxybenzyl alcohol (A and B) and 3,4-dimethoxybenzoic acid (C). The benzoic acid did not form any apparent adducts with TMP (δ 140 to -50 ppm monitored) and is shown as a blank spectrum. Clearly, in the blank spectrum (Figure 8C) TMP degradation products are observed, including: dimethylphosphite (VII, Figure 5) and methylphosphate esters (δ 3.5 (VIII), 1.8, and 0.8 ppm).

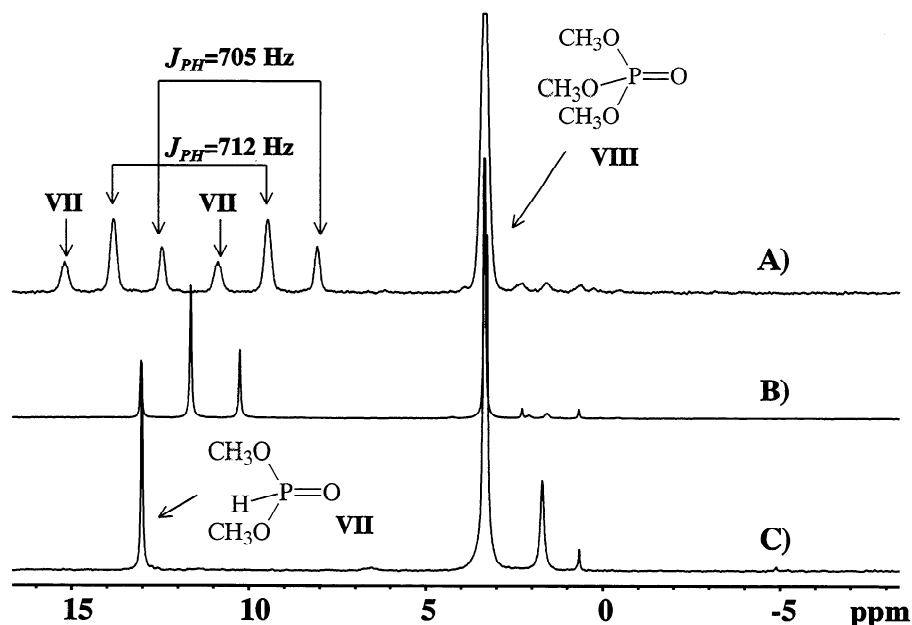


Figure 8. ^{31}P -NMR spectra of TMP treated compounds: 3,4-dimethoxybenzyl alcohol A) ^1H coupled, B) ^1H decoupled and C) 3,4-dimethoxybenzoic acid ^1H decoupled.

Hoffmann [90] and others [71, 91, 92] have noted that trialkylphosphites can undergo transesterification with alcohols. Figure 9 illustrates a pathway of TMP benzylalcohol exchange with subsequent hydrolysis of the mixed trialkylphosphite. Note, the ^1H decoupled spectrum of 3,4-dimethoxybenzyl alcohol shows the appearance of two new resonances after TMP treatment and hydrolysis (δ 11.6 and 10.2 ppm, Figure 8B). These signals were tentatively assigned to hydrogen-phosphites formed from single (XIX, Figure 9) and multiple exchange reactions. The assignment of this structure type is strongly supported by ^{31}P - ^1H coupling constant data (~ 700 Hz, Figure 8A).

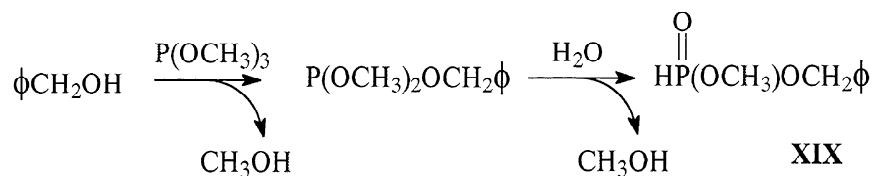


Figure 9. Alcohol exchange reaction between TMP and benzyl alcohol.

Figure 10 reveals the presence of hydrogen-phosphite structures in TMP-derivatized chlorine dioxide residual lignin. Adducts can be identified in the ^1H coupled

spectra (Figure 10A) as hydrogen–phosphites ($^1J_{PH} = 716$ Hz), possibly derived from lignin hydroxyl groups such as benzyl alcohol. The lignin polymer is much less mobile than the small molecule benzyl alcohol, hence, only a single alcohol exchange reaction is most likely to occur. Interestingly, the chemical shift of the hydrogen–phosphite product is coincident with cyclic phosphate adducts expected from TMP derivatized *ortho*–quinones ($\delta \sim 12$ ppm, see Figure 2). But, ^{31}P – ^1H spin coupling data excludes the possibility that the $\delta \sim 12$ ppm signal can be assigned to an *ortho*–quinone derived cyclic phosphate ester.

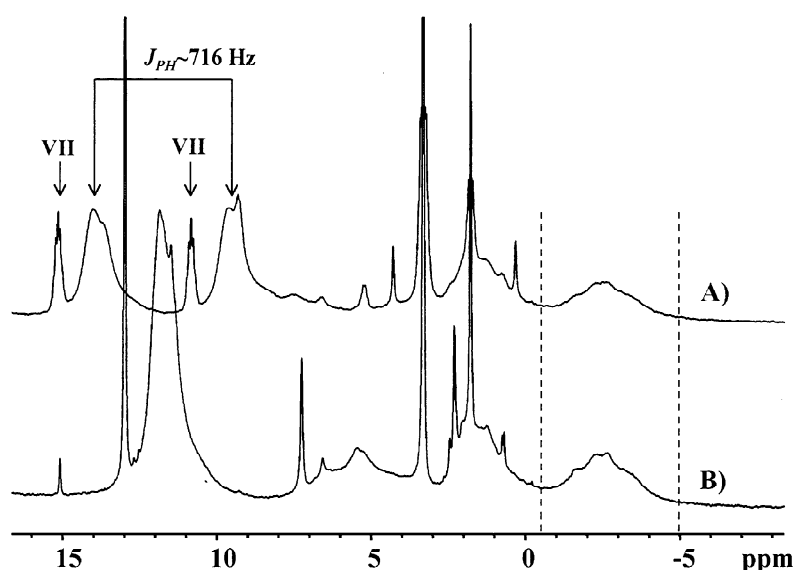


Figure 10. ^{31}P –NMR spectra of TMP treated D_0 residual lignin: A) ^1H coupled and B) ^1H decoupled.

Conclusions

Trimethylphosphite derivatization and ^{31}P –NMR spectroscopy has proved useful for a study of the introduction and removal of colored benzoquinone structures during kraft pulp bleaching. Chlorine dioxide bleaching dramatically increased lignin–quinone content whereas subsequent alkaline extraction reduced the content. Oxygen delignification also resulted in quinone formation, but to a lesser extent than with chlorine dioxide. Peracetic acid displayed a beneficial effect by eliminating quinone structures. Consistent with known chemistry, trimethylphosphite in the presence of water gave drastically lower

derivatization yield for an isolated chlorine dioxide residual lignin. The optimum derivatization treatment time for isolated lignin in anhydrous DMF solution was found to be approximately two days.

The fundamental chemistry of TMP derivatization of lignin was explored using quinone model compounds, 3,4-dimethoxybenzyl alcohol, and 3,4-dimethoxybenzoic acid. Both *ortho*- and *para*-benzoquinone model compounds were found to give dimethylphosphate ester products consistent with our previous studies and literature reports. 3,4-Dimethoxybenzoic acid was found to be unreactive with trimethylphosphite. Conversely, 3,4-dimethoxybenzyl alcohol gave dialkylhydrogen phosphite adducts after transesterification with trimethylphosphite and subsequent hydrolysis.

Derivatization yields for quinone model compounds were generally high; cases of incomplete derivatization may be explained by competing self-dimerization and degradation reactions. Hence, some monomeric thermally unstable quinone model compounds are not effective models for benzoquinone structures in isolated lignins. A model polymeric *ortho*-quinone was prepared by the oxidation of poly(4-vinylphenol) and characterized by trimethylphosphite/ ^{31}P -NMR spectroscopy. Therefore, the developed method may have broader applicability for the study of quinone structures in other aromatic and phenolic polymers.

Major degradation products of the derivatization reagent, TMP, were identified by ^{31}P -NMR chemical shifts and ^{31}P - ^1H coupling constants. Dimethylphosphite was found to cause difficulty with trace lignin-quinone analysis. The negative influence of dimethylphosphite was substantially reduced by removing the volatile compound using vacuum and heat and using classical high-power broadband decoupling ^1H decoupled during NMR acquisition.

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List of Abbreviations

BS = brownstock, unbleached pulp
Cr(acac)₃ = chromium–acetylacetonate
D₀, D = chlorine dioxide bleached pulp
DMF = dimethylformamide
DMSO = dimethylsulfoxide
KF = kappa factor
O = oxygen delignified pulp
ortho–benzoquinone = 1,2–benzoquinone
Pa = peracetic acid bleached pulp
para–benzoquinone = 1,4–benzoquinone
PVP = poly(4-vinylphenol)
SW = softwood kraft pulp
T₁ = spin–lattice relaxation
TMP = trimethylphosphite
TTP = tri–*meta*–tolylphosphate

References

- [1] Hartler, N. and Norrstrom, H., "Light-Absorbing Properties of Pulp and Pulp Components III. Kraft Pulp", *TAPPI Journal*, 52 (9), 1712, (1969)..
- [2] Gierer, J., "Chemistry of Delignification. Part 1: General Concepts and Reactions During Pulping", *Wood Science and Technology*, 19, 289, (1985).
- [3] Gierer, J., "Chemistry of Delignification, Part 2: Reactions of Lignins During Bleaching", *Wood Science and Technology*, 20, 1, (1986).
- [4] Gierer, J., "Basic Principles of Bleaching, Part 1: Cationic and Radical Processes", *Holzforschung*, 44 (5), 387, (1990).
- [5] Gierer, J., "The Reactions of Lignin During Pulping: A Description and Comparison of Conventional Pulping Processes", *Svensk Papperstidning*, 18, 571, (1970).

- [6] Polcin, J. and Rapson, W., "The Interpretation of UV and Visible Spectrum of Lignin", *Pulp and Paper Magazine of Canada*, 12, 99, (1969).
- [7] Glasser, W. and Hon, D., "On Possible Chromophoric Structures in Wood and Pulps – Survey of Present State of Knowledge", *Polymer-Plastics Technology Engineering*, 12 (2), 159, (1979).
- [8] Lonsky, L., Lonsky, W., and Kratzl, K., "Synthesis and Reactions of Hydroxylated Stilbenes and Their Possible Occurrence as Chromophore Precursor Structures in Lignin", *Monatshefte fur Chemie*, 107, 685, (1976).
- [9] Furman, G. and Lonsky, F., "Charge-Transfer Complexes in Kraft Lignin. Part (2) Contribution to Color", *Journal of Wood Chemistry and Technology*, 8 (2), 191, (1988).
- [10] Polcin, J. and Rapson, W., "Effects of Bleaching Agents on the Absorption Spectra of Lignin in Groundwood Pulps: Part 1. Reductive Bleaching", *Pulp and Paper Magazine of Canada*, 72 (3), 69, (1971).
- [11] Iiyama, K. and Nakano, J., "Studies on the Color of Lignin. Part X. Effects of Chromophoric Groups on the Color of Various Lignins", *Japan TAPPI*, 27 (11), 530, (1973).
- [12] Berger, S. and Rieker, A., *Identification and Determination of Quinones*, in *The Chemistry of Quinonoid Compounds*, Patai, S., Editor, John Wiley and Sons, New York, p 163, (1974).
- [13] Paulsson, M., Li, S., Lundquist, K., Simonson, R., and Westermarck, U., "Chemical Modification of Lignin-Rich Paper. Part 4. Elimination of Chromophoric and Leucochromophoric Structures by Acetylation", *Nordic Pulp and Paper Research Journal*, 4, 220, (1996).
- [14] Imsgard, F., Falkehag, S., and Kringstad, K., "On Possible Chromophoric Structures in Spruce Wood", *TAPPI Journal*, 54 (10), 1680, (1971).
- [15] Hayashi, A., Kinoshita, K., and Taniguchi, A., "Demethylation of Lignin During Pulping. III. Correlation Between Oxidation Product of Quinones and Lignin Chromophores", *Mokuzai Gakkaishi*, 21 (8), 485, (1975).
- [16] Hayashi, A., Kinoshita, K., and Taniguchi, A., "Demethylation of Lignin During Pulping. II. Correlation Between Demethylation and Coloring with Soda Cooking", *Mokuzai Gakkaishi*, 21 (8), 480, (1975).
- [17] Brage, C., Eriksson, T., and Gierer, J., "Reactions of Chlorine Dioxide with Lignins in Unbleached Pulps. Part I", *Holzforschung*, 45, 23, (1991).
- [18] Brage, C., Eriksson, T., and Gierer, J., "Reactions of Chlorine Dioxide with Lignins in Unbleached Pulps. Part II", *Holzforschung*, 45, 147, (1991).
- [19] Lindgren, B., "Chlorine Dioxide and Chlorite Oxidations of Phenols Related to Lignin", *Svensk Papperstidning*, 3, 57, (1971).
- [20] Gellerstedt, G., Pettersson, I., and Sundin, S.E., "Chemical Aspects of Hydrogen Peroxide Bleaching", Proceedings, International Symposium on Wood and Pulping Chemistry, Stockholm, Sweden, June 9-12, 1981, p. 120.

- [21] Zawadzki, M., Runge, T., and Ragauskas, A., "Chromophore Properties of High Brightness Pulps", Proceedings, TAPPI Pulping Conference, Montreal, Canada, October 25-29, 1998, p. 1551.
- [22] Zawadzki, M., Runge, T., and Ragauskas, A., *Investigation of Ortho- and Para-Quinone Chromophores in Alkaline Extraction Stage Residual Lignins*, in *Lignins: Historical, Biological, and Materials Aspects*, Glasser, W., Northey, R., and Schultz, T., Editors, American Chemical Society, (1999).
- [23] Zakis, G., *Functional Analysis of Lignins and Their Derivatives*, TAPPI Press, Atlanta, GA, 1994.
- [24] Norrstrom, H., "Spectra of Lignins from Pulp and Spent Liquor", *Svensk Papperstidning*, 19 (15), 619, (1970).
- [25] Zhu, J., Olmstead, J., and Gray, D., "Fluorescent Detection of *o*-Quinones Formed in Lignin-Containing Pulps During Irradiation", *Journal of Wood Chemistry and Technology*, 15 (1), 43, (1995).
- [26] Mislankar, A., Darabie, A., and Reeve, D., "Detection of *Ortho*-Quinones in Wood Using Confocal Laser Scanning Microscopy", *Journal of Pulp and Paper Science*, 23 (2), J73, (1997).
- [27] Sevillano, R., Barrelle, M., Mortha, G., and Lachenal, D., "¹⁹F-NMR Spectroscopy for the Quantitative Analysis of Carbonyl Groups in Lignin", Proceedings, International Symposium on Wood and Pulping Chemistry, Yokohama, Japan, 1999, p. 28.
- [28] Zawadzki, M. and Ragauskas, A., "Pulp Properties Influencing Oxygen Delignification Bleachability", Proceedings, TAPPI Pulping Conference, Orlando, November 1-3, 1999, p. submitted.
- [29] Ahvazi, B., Crestini, C., and Argyropoulos, D., "¹⁹F NMR Spectroscopy for the Quantitative Detection and Classification of Carbonyl Groups in Lignins", Proceedings, International Symposium on Wood and Pulping Chemistry, Yokohama, Japan, 1999, p. 34.
- [30] Ahvazi, B. and Argyropoulos, D., "¹⁹F Nuclear Magnetic Resonance Spectroscopy for the Elucidation of Carbonyl Groups in Lignins. I. Model Compounds", *Journal of Agriculture and Food Chemistry*, 44, 2167, (1996).
- [31] Lebo, S., Lonsky, W., McDonough, T., Medvecz, P., and Dimmel, D., "The Occurrence and Light-Induced Formation of *Ortho*-Quinoid Lignin Structures in White Spruce Refiner Mechanical Pulp", *Journal of Pulp and Paper Science*, 16 (5), J139, (1990).
- [32] Lebo, S., Lonsky, W., and McDonough, T., "The Occurrence and Light Induced Formation of *Ortho*-Quinoid Lignin Structures in White Spruce Refiner Mechanical Pulp", Proceedings, International Pulp Bleaching Conference, Orlando, June 5-9, 1988, p. 247.
- [33] Konya, K. and Scaiano, J., "Development and Application of Pyrene-Containing Fluorescent Probes for Monitoring the Photodegradation of Lignin-Rich Products", *Chemistry of Materials*, 6, 2369, (1994).

- [34] Argyropoulos, D., Heitner, C., and Morin, F., "³¹P-NMR Spectroscopy in Wood Chemistry Part III. Solid State ³¹P-NMR of Trimethyl Phosphite Derivatives of Chromophores in Mechanical Pulp", *Holzforschung*, **46** (3), 211, (1992).
- [35] Argyropoulos, D. and Heitner, C., "³¹P NMR Spectroscopy in Wood Chemistry. Part VI. Solid State ³¹P NMR of Trimethyl Phosphite Derivatives of Chromophores and Carboxylic Acids Present in Mechanical Pulps; A Method for the Quantitative Determination of Ortho-Quinones.", *Holzforschung*, **48**, 112, (1994).
- [36] Argyropoulos, D. and Zhang, L., "Semiquantitative Determination of Quinoid Structures in Isolated Lignins by ³¹P Nuclear Magnetic Resonance", *Journal of Agriculture and Food Chemistry*, **46**, 4628, (1998).
- [37] Zawadzki, M., Runge, T., and Ragauskas, A., "Facile Detection of Ortho- and Para-Quinone Structures in Residual Kraft Lignin by ³¹P-NMR Spectroscopy", *Submitted to the Journal of Pulp and Paper Science*, , (1998).
- [38] Zhang, L. and Gellerstedt, G., "Quinone Chromophores and their Contribution to Photo-Yellowing in Lignin", *Proceedings, Fifth European Workshop on Lignocellulosics and Pulp*, 1998, p. 285.
- [39] Zhang, L. and Gellerstedt, G., "Detection and Determination of Carbonyls and Quinones by Modern NMR Techniques", *Proceedings, International Symposium on Wood and Pulp Chemistry*, Yokohama, Japan, 1999, p. 164.
- [40] Cason, J., *Chapter 6: Synthesis of Benzoquinones by Oxidation*, in *Organic Reactions, Volume 4*, Adams, R., Editor, John Wiley and Sons, New York, (1948).
- [41] Wozniak, J., Dimmel, D., and Malcolm, E., "The Generation of Quinones from Lignin and Lignin-Related Compounds", *Journal of Wood Chemistry and Technology*, **9** (4), 491, (1989).
- [42] Froass, P., Ragauskas, A., McDonough, T., and Jiang, J., "Relationship Between Residual Lignin Structure and Pulp Bleachability", *Proceedings, International Pulp Bleaching Conference*, Washington, D.C., June, 1996, p. 163.
- [43] Moe, S., Ragauskas, A., and McDonough, T., "Extended Oxygen Delignification of High-Yield Kraft Pulp. Correlation Between Residual Lignin Structures and Bleachability by Oxygen and Chlorine Dioxide", *Proceedings, International Pulp Bleaching Conference*, Helsinki, Finland, 1998, p. 33.
- [44] Pepper, J., Baylis, P., and Alder, E., "The Isolation and Properties of Lignins Obtained by the Acidolysis of Spruce and Aspen Woods in Dioxane-Water Medium", *Canadian Journal of Chemistry*, **37**, 1241, (1959).
- [45] Ramirez, F. and Dershowitz, S., "Paramagnetic Resonance Absorption and New Types of Group Translocations in the Reaction of Trialkyl Phosphite with Chloranil", *Journal of Organic Chemistry*, **22**, 856, (1957).
- [46] Ramirez, F., "Condensation of Carbonyl Compounds with Phosphite Esters", *Pure and Applied Chemistry*, **9**, 337, (1964).
- [47] Ramirez, F., "Syntheses via Oxyphosphoranes", *Synthesis*, **90**, (1974).

- [48] Abdou, W., Mahran, M., Hafez, T., and Sidky, M., "The Reaction of Alkyl Phosphites with 3,5-di-*tert*-butyl-1,2-benzoquinone. Variable Temperature NMR Studies on Pentaoxyphosphoranes", *Phosphorus and Sulfur*, **27**, 345, (1986).
- [49] Boeckstein, G., Voucken, W., Jansen, E., and Buck, H., "Electron Transfer Reactions Between Trivalent Phosphorus Compounds and Activated Ketones", *Recueil des Travaux Chimiques des Pays-Bas*, **93**, 69, (1974).
- [50] Medvecz, P., "The Reactions Of *Ortho*- and *Para*-Quinonoid Lignin Model Compounds with Alkyl Phosphites and Alkyl Phosphines", M.S. Thesis, Institute of Paper Science and Technology, Atlanta, (1987).
- [51] Ramirez, F., Mitra, R., and Desai, N., "A Carbon-Skeleton Rearrangement During The Oxidative Dephosphorylation of a New Type of Phosphorus Compound. Reaction of Molecular Oxygen with the Crystalline 1:1 Adduct Derived From Tertiary Phosphite Esters and Alpha-Diketones", *Journal of the American Chemical Society*, **82**, 2651, (1960).
- [52] Ramirez, F., Patwardhan, A., Desai, N., and Heller, S., "The Hydrolysis of Five-Membered Cyclic Oxyphosphoranes to Cyclic Phosphate Esters. ³¹P Nuclear Magnetic Resonance and Stereoisomerism at Phosphorus in Cyclic Phosphates", *Journal of the American Chemical Society*, **87** (3), 549, (1965).
- [53] Ramirez, F., Ramanathan, N., and Desai, N., "Cyclic Saturated Oxyphosphoranes and Their Hydrolysis to Cyclic Phosphate Esters. The Diastereomeric 2:1 Biacetyl-Trimethyl Phosphite Adducts", *Journal of the American Chemical Society*, **85** (3465-3472), (1963).
- [54] Blackburn, G., Cohen, J., and Todd, L., "Cyclic Phosphate and Phosphate Triesters, A ³¹P-NMR Study", *Tetrahedron Letters*, **39**, 2873, (1964).
- [55] Ramirez, F., Kugler, H., Patwardhan, A., and Smith, C., "α,β-Unsaturated Aldehydes as Acceptors in the Oxyphosphorane Carbon-Carbon Condensation. Hydrolyses of Five-Membered Cyclic Pentaoxyphosphoranes and Phosphate Esters", *Journal of the American Chemical Society*, **33** (3), 1185, (1968).
- [56] Ramirez, F., Kugler, H., and Smith, C., "Nucleophilic 1,2-Additions to the Carbonyl Group of *p*-Quinones. Hydrolysis and Alcoholysis of the Pentaoxyphosphoranes Derived from the Condensation of α-Diketones with *p*-Quinones by Means of Trialkyl Phosphites", *Tetrahedron*, **24** (4), 1931, (1968).
- [57] Kirillova, K. and Kukhtin, V., "Some New Forms of the Arbuzov Rearrangement. XVI. Addition of Trialkyl Phosphites to 1,2-Naphthoquinone", *Zhurnal Obshchei Khimii*, **32** (7), 2338, (1962).
- [58] Gorenstein, D., Schroeder, S., Miyasaki, M., Fu, J., Roongta, V., Abuaf, P., Metz, J., and Jones, C., "³¹P NMR and Two-Dimensional NMR Spectra of Nucleic Acids and 2D NOESY-Constrained Molecular Mechanics Calculations for Structural Solution of Duplex Oligonucleotides", *Bulletin of Magnetic Resonance*, **8**, 137, (1986).
- [59] Abdou, W., Salem, M., and Sediek, A., "Comparative Behavior of 2,6-di-*tert*-Butyl- and 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone with Some Phosphorus Reagents", *Journal of Chemical Research (S)*, **28**, (1998).

- [60] Ramirez, F., Bhatia, S., Patwardhan, A., Chen, E., and Smith, C., "Reactions of Trialkyl-Phosphites with Polycyclic *p*- and *o*-Quinones. Anthraquinone, the Pyrenequinones, and the Naphthoquinones", *Journal of Organic Chemistry*, **33** (1), 20, (1968).
- [61] Ramirez, F. and Dershowitz, S., "Trialkyl Phosphites as Reagents in a Novel Reductive O-Alkylation of Quinones", *Journal of the American Chemical Society*, **23**, 778, (1958).
- [62] Lewis, E. and Colle, K., "Alkoxyphosphonium Salts. 3. Kinetics and Thermodynamics in Alkylation by Alkylphosphonium Salts", *Journal of the American Chemical Society*, **46**, 4369, (1981).
- [63] Mahran, M., Abdou, W., and Hafez, T., "The Reaction of Alkyl Phosphite with Asymmetric *p*-Quinone Kheliquinone and Psoralenequinone", *Egyptian Journal of Chemistry*, **24** (6), 401, (1981).
- [64] Sidky, M., Mahran, M., and El-Khoshnieh, Y., "Organophosphorus Compounds XIX The Reaction of Trialkyl Phosphites with Extended *p*-Quinones", *Tetrahedron*, **30**, 47, (1974).
- [65] Forsskahl, I., Gustafsson, J., and Nybergh, A., "The Photochemical Discoloration of Methoxy-*p*-benzoquinone in solution", *Acta Chemica Scandinavica*, **B35**, 389, (1981).
- [66] Horspool, W., "Synthetic 1,2-Quinones: Synthesis and Thermal Reactions", *Quarterly Reviews*, **23**, 204, (1969).
- [67] Jacques, B., Devaux, J., Legras, R., and Nield, E., "Investigation on Model Molecules of the Reactions Induced by Triphenylphosphite Addition During Polyester Processing", *Macromolecules*, **29**, 3129, (1996).
- [68] Huyser, E. and Dieter, J., "Synthesis and Acetolysis of Mixed Trialkyl Phosphites", *Journal of Organic Chemistry*, **33** (11), 4205, (1968).
- [69] Aksnes, G. and Aksnes, D., "Kinetics and Mechanism of the Reaction of Tripropyl Phosphite with Water in Acetonitrile", *Acta Chemica Scandinavica*, **18**, 1623, (1964).
- [70] Hudson, R., *Structure and Mechanism in Organo-Phosphorus Chemistry*, Academic Press, New York, 1965.
- [71] Gay, I., McFarlan, A., and Morrow, B., "Trimethyl Phosphite Adsorbed on Silica: An NMR and Infrared Study", *Journal of Physical Chemistry*, **95**, 1360, (1991).
- [72] Ogata, Y. and Yahashita, M., "Autoxidation of Trimethyl Phosphite Initiated by One-Electron Transfer from Phosphite to Quinones", *Bulletin of the Chemical Society of Japan*, **46** (7), 2208, (1973).
- [73] Gallagher, M., *Fully Coupled Spectra in the Analysis of Reaction Mixtures*, in *Phosphorous-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*, Quin, L. and Verkade, J., Editors, VCH, New York, p 385, (1994).
- [74] Tebby, J., *CRC Handbook of Phosphorus-31 Nuclear Magnetic Resonance Data*, CRC Press, Boca Raton, (1991).

- [75] Crutchfield, M., Dungan, C., and Van Wazer, J., *The Measurement and Interpretation of High-Resolution P31 Nuclear Magnetic Resonance Spectra*, in *Topics in Phosphorous Chemistry, Volume 5*, Interscience, p 1, (1967).
- [76] Marvin, M., Crutchfield, M., Dungan, C., and Van Wazer, J., *The Measurement and Interpretation of High-Resolution P31 Nuclear Magnetic Resonance*, in *Topics in Phosphorus Chemistry, Volume Five, P31 Nuclear Magnetic Resonance*, Grayson, M. and Griffith, E., Editors, Interscience, New York, (1967).
- [77] Thomas, L., *The Identification of Functional Groups in Organophosphorus Compounds*, Academic Press, London, (1974).
- [78] Gorenstein, D., *Chapter 2, Phosphorus-31 Spin-Spin Coupling Constants: Principles and Applications*, in *Nuclear Magnetic Resonance, Volume 5*, Harris, R., Editor, The Chemical Society, London, p 37, (1976).
- [79] Shaka, A., Keeler, J., and Freeman, R., "Evaluation of a New Broadband Decoupling Sequence: Waltz-16", *Journal of Magnetic Resonance*, 53, 313, (1983).
- [80] Wink, D., "Spin-Lattice Relaxation Times in ^1H NMR Spectroscopy", *Journal of Chemical Education*, 66 (10), 810, (1989).
- [81] Ejchart, A., Oleski, P., and Wroblewski, K., "Separation of Intra and Intermolecular ^{31}P - ^1H Dipolar Interactions in Phosphonates by Way of T_1 Measurements of ^{31}P Nuclei", *Polish Journal of Chemistry*, 59, 845, (1985).
- [82] Froass, P., "Structural Changes in Lignin During Kraft Pulping and Chlorine Dioxide Bleaching", Ph.D. Thesis, Institute of Paper Science and Technology, Atlanta, (1996).
- [83] McKague, A.B., Kang, G.J., and Reeve, D.W., "Reaction of a Lignin Model Dimer with Chlorine Dioxide", *Holzforschung*, 47, 497, (1993).
- [84] McKague, A.B., Kang, G.J., and Reeve, D.W., "Reactions of Lignin Model Dimers with Chlorine Dioxide", *Nordic Pulp and Paper Research Journal*, 9 (2), 84, (1994).
- [85] McKague, A.B., Reeve, D.W., and Xi, F., "Reactions of Model Compounds Sequentially with Chlorine Dioxide and Sodium Hydroxide", *Nordic Pulp and Paper Research Journal*, 10 (2), 114, (1995).
- [86] Ni, Y., Shen, X., and van Heiningen, A., "Studies on the Reactions of Phenolic and Non-Phenolic Lignin Model Compounds with Chlorine Dioxide", *Journal of Wood Chemistry and Technology*, 14 (2), 243, (1994).
- [87] Leary, G. and Giampaolo, D., "The Darkening Reactions of TMP and BTMP During Alkaline Peroxide Bleaching", *Journal of Pulp and Paper Science*, 25 (4), 141, (1999).
- [88] McDonough, T. and Rapson, W., "Reactions of Peracetic Acid with Lignin Model Compounds in Alkaline Solution", *CPPA Transactions of the Technical Section*, 1 (1), 12, (1975).

- [89] Factor, A. and Donahue, P., "The Use of ^{31}P -NMR to Identify Color Bodies in G-Irradiated Bisphenol-A Polycarbonate", *Polymer Degradation and Stability*, 57, 83, (1997).
- [90] Hoffman, F., Ess, R., and Usinger, R., "The Transesterification of Trialkyl Phosphites with Aliphatic Alcohols", *Journal of the American Chemical Society*, 78, 5817, (1956).
- [91] Oza, V. and Corcoran, R., "A Mild Preparation of Protected Phosphate Esters from Alcohols", *Journal of Organic Chemistry*, 60, 3680, (1995).
- [92] Batyeva, E., Al'fonsov, V., and Pudovik, A., *Chapter 3. Acid Catalysis in Reactions of Derivatives of Trivalent Phosphorus Acids*, in *Advances in Sciences and Technology in the USSR, Chemistry Series, Chemistry of Organophosphorus Compounds*, Pudovik, A., Editor, MIR Publishers, Moscow, Russia, p 68, (1989).

